



Influence of oxygen addition on photocatalytic oxidation of aqueous ammonia over platinum-loaded TiO₂



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ABSTRACT

The oxidation of aqueous ammonia over a platinum-loaded TiO₂ photocatalyst was investigated for purification of wastewater. The reaction rate for the decomposition of aqueous ammonia was significantly increased by the addition of oxygen to the reaction system. The enhancement of charge separation efficiency due to consumption of photogenerated electrons by oxygen increased the decomposition rate. For dissolved oxygen (DO) concentrations below 0.09 mM, the initial decomposition rate and the selectivity for nitrite and nitrate increased as DO concentration increased. Although the selectivity for nitrite and nitrate was over 90% for the initial concentration of ammonia ([NH₃]_i) = 5.0 mM under an air flow, the selectivity was suppressed as the initial concentration of ammonia was increased, e.g., 43% for [NH₃]_i = 100 mM.

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1. Introduction

Wastewater containing ammonia is discharged from different types of facilities such as livestock production facilities, heat power plants, chemical facilities and sewage farms. Since ammonia is a source of nutrients that may accelerate the eutrophication of lake water and inland sea areas, its removal from wastewater is important from an environmental perspective.

Several methods have been developed and applied to the treatment of ammonia-containing wastewater, including biological processes, air stripping, ion exchange, breakpoint chlorination, and chemical oxidation [1,2]. Among these methods, biological processes are generally regarded to be the most efficient. However, these processes have disadvantages, including handling difficulties and large equipment requirements. Moreover, they are difficult to apply to treatment of wastewater that contains harmful co-existing species for bacteria. In the case of air stripping or ion exchange, ammonia/ammonium ions can be eliminated from wastewater, but treatment of the removed ammonia/ammonium ions is still required. Although breakpoint chlorination can convert aqueous ammonia to nitrogen, the formation of harmful by-products must be suppressed and treatment of residual chlorine is required. Catalytic wet oxidation of ammonia has been reported, in which the treatment is conducted under relatively high pressures and temperatures, e.g., 2.0 MPa and 500 K [3].

Photocatalytic oxidation using TiO₂ is used for the purification of wastewater containing organic pollutants (e.g., herbicides,

fungicides) [4], inorganic ions (e.g., sulfide, cyanide), etc. There have been several studies on the photocatalytic oxidation of ammonia using TiO₂ and/or Pt-TiO₂ as a method for purifying wastewater [5–10]. Some studies showed the effect of pH, the photocatalytic oxidation of ammonia in water proceeds under alkaline conditions [5–9], while others revealed the optimum concentration of TiO₂ in the reaction solution [5,9], the effect of platinum loading on TiO₂ [8], or the effect of inorganic anions [10]. In these studies, the initial concentrations of ammonia in the reaction solution were on the order of ppm, and relatively long reaction times were required for the decomposition of ammonia. For these reasons, application of this method to the treatment of wastewater that contains high concentrations of ammonia is difficult. On the other hand, photocatalytic decomposition of ammonia in the gas phase over TiO₂ has been reported [11–13]. Yamazoe et al. and Mozzanega et al. showed that the partial pressure of oxygen strongly affects the decomposition rate of ammonia [11,13].

In the present study, we investigated the photodecomposition of a reaction system consisting of Pt-TiO₂ and aqueous ammonia, and determined the influence of the addition of oxygen to the reaction system on the photodecomposition rate of aqueous ammonia and also on the selectivity for nitrite and nitrate. The formation of nitrite and nitrate must be minimized since they are also major N-containing pollutants.

2. Experimental

2.1. Materials

Platinum-loaded TiO₂ was used as the photocatalyst. The TiO₂ (ST-01, anatase, Ishihara Sangyo Co., Ltd.) used in the reaction had

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a BET surface area of $303 \text{ m}^2 \text{ g}^{-1}$ and an average particle size of 7 nm. Platinum (0.5 wt%) was loaded onto TiO_2 by photochemical reduction of tetrachloroplatinate in a TiO_2 suspension in the presence of 1.2 M methanol. The amount of platinum loaded on TiO_2 was confirmed by ICP measurement of the platinum remaining in solution.

2.2. Photocatalytic reaction and analysis

The photocatalytic reactions were carried out in an inner irradiation reaction cell made of Pyrex glass. A high-pressure mercury lamp (Ushio UM-452, 450 W) was employed as the light source. Pt- TiO_2 (0.2 g) or TiO_2 (0.2 g) was suspended in 400 mL of ammonium sulfate aqueous solution with a magnetic stirrer. The sulfate ions do not affect the decomposition rate under the conditions used in this study. The initial pH was adjusted to 12 by the addition of sodium hydroxide aqueous solution in order to maintain the alkaline condition during the reaction, since the pH of the reaction solution decreases as the reaction proceeds and the reaction only proceeds under alkaline conditions. Air or a nitrogen/oxygen mixture (partial pressure of oxygen (P_{O_2}) = 0–0.1 MPa) was introduced into the reaction suspension using a mass flow controller (Kofloc Model 3200) with a Teflon tube (inside diameter 2 mm). Gas flow was initiated for 60 min prior to the reaction to purge the dissolved gas. The temperature of the reaction solution during the photocatalytic reaction was about 298–300 K. The concentrations of nitrate, nitrite and ammonia in the aqueous phase were measured using a flow injection analysis system consisting of a JASCO UV-2070 detector and a UV-2075 detector equipped with a PU-2080 pump. Although dinitrogen and dinitrogen monoxide are the presumed products of this reaction, the concentrations of these species were not measured during most of this study since the process was difficult. Hydroxylamine was not detected by capillary electrophoresis in this study. The amount of dissolved oxygen (DO) in the reaction mixture was measured using a dissolved oxygen meter (Lutron DO-5509). The initial decomposition rate was calculated by the extrapolation method.

3. Results and discussion

3.1. Influence of oxygen addition on ammonia photocatalytic oxidation

The time courses of ammonia and DO concentrations in the presence of 0.5 wt% Pt- TiO_2 under an air or nitrogen flow rate of $100 \text{ cm}^3 \text{ min}^{-1}$ and without gas flow (under air atmosphere) are shown in Fig. 1. When the reaction was conducted without gas flow, the concentration of ammonia decreased slowly and linearly with reaction time. The initial rate of decrease of ammonia was $6.0 \mu\text{M min}^{-1}$ under this condition. The concentration of DO was 0.24 mM at the beginning of the reaction, and it decreased immediately to less than 0.02 mM, indicating that oxygen was consumed during the reaction. Under the condition of N_2 flow, the rate of ammonia decrease was slightly smaller than that without gas flow. In contrast, when the reaction was performed under air flow, the decrease in the concentration of ammonia was much faster than that under N_2 flow and without gas flow. The initial rate of decrease of ammonia was $37 \mu\text{M min}^{-1}$ under air flow. Although the DO concentration temporarily decreased to about 0.15 mM, it gradually recovered and then stayed constant at about 0.24 mM.

It is well known that ammonia volatilizes when gas is bubbled through alkaline solutions [14]. However, in the present study, for ammonia concentrations of 5–100 mM (adjusted pH 12) in the absence of the photocatalyst under UV irradiation and an air flow rate of $100 \text{ cm}^3 \text{ min}^{-1}$, the decrease in the ammonia concentration

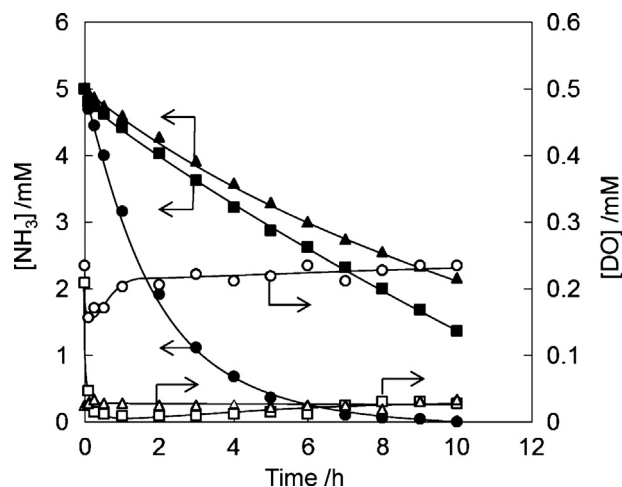


Fig. 1. Time courses of ammonia (closed symbols) and DO (open symbols) concentrations in the presence of 0.5 wt% Pt- TiO_2 under air or nitrogen flow and without gas flow (under air atmosphere). Circles: under air flow; triangles: under nitrogen flow; squares: without gas flow.

in solution was small. This indicated that volatilization of ammonia into the atmosphere was negligible under the reaction conditions used in this study. The fact that the rate of decrease in the ammonia concentration under N_2 flow was smaller than that without gas flow as shown in Fig. 1 also indicated that there was almost no influence of volatilization. The experiment performed without UV irradiation and in the presence of 0.2 g of Pt- TiO_2 showed that the adsorption amount of ammonia onto the Pt- TiO_2 surface was negligible. Furthermore, a decrease in the ammonia concentration and an increase in nitrate and nitrite concentrations were not observed under air flow in the absence of Pt- TiO_2 , indicating that the decomposition of aqueous ammonia by UV irradiation did not occur under this condition. Therefore, the decrease in ammonia concentration shown in Fig. 1 must be due to photocatalytic decomposition and not volatilization, adsorption on the surface of the photocatalyst, or photodecomposition in the absence of the photocatalyst.

Fig. 2 shows plots of nitrate and nitrite concentrations versus time for the same run with Fig. 1. The concentration of nitrite increased with irradiation time under N_2 flow and without gas flow. Under air flow, it increased in the first 4 h and then decreased. The concentration of nitrate increased with time under each condition.

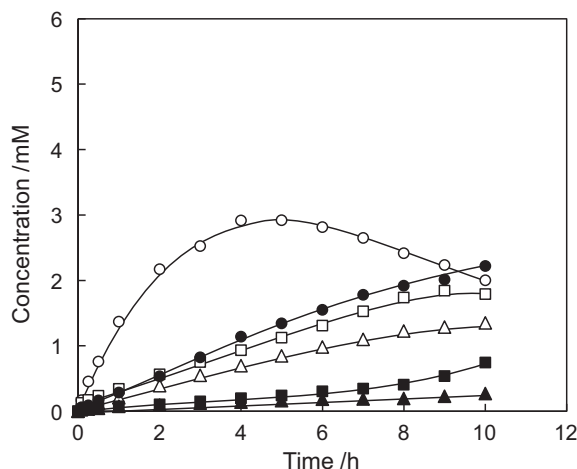


Fig. 2. Time courses of nitrite and nitrate concentrations in the presence of 0.5 wt% Pt- TiO_2 under air or nitrogen flow and without gas flow (under air atmosphere). Open symbols: nitrite; closed symbols: nitrate. Circles: under air flow; triangles: under nitrogen flow; squares: without gas flow.

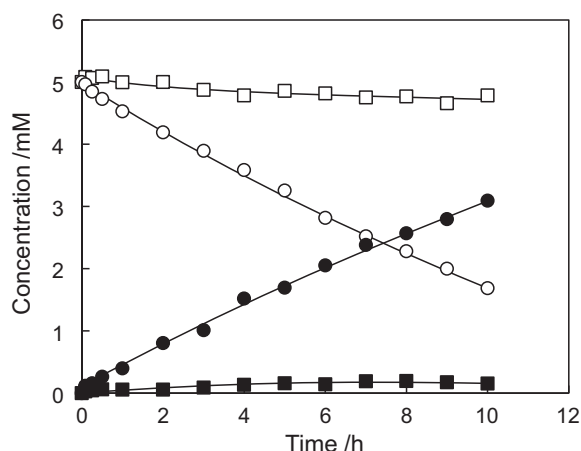


Fig. 3. Time courses of nitrite and nitrate concentrations under UV irradiation and air flow in the presence or absence of 0.5 wt% Pt-TiO₂. Circles: in the presence of 0.5 wt% Pt-TiO₂; squares: in the absence of 0.5 wt% Pt-TiO₂; open symbols: nitrite; closed symbols: nitrate.

Fig. 3 shows the time courses of nitrite and nitrate concentrations under UV irradiation and air flow in the presence or absence of Pt-TiO₂. In the presence of Pt-TiO₂, the concentration of nitrite gradually decreased, while the concentration of nitrate increased. The increased amount of nitrate was in accordance with the decreased amount of nitrite. On the other hand, almost no decomposition of nitrite was observed when the reaction was conducted in the absence of Pt-TiO₂. Therefore, nitrite that formed by the oxidation of ammonia decomposed photocatalytically on Pt-TiO₂ to form nitrate.

3.2. Role of oxygen for enhancement of ammonia decomposition rate

As shown in Fig. 1, oxygen has a strong influence on the photocatalytic decomposition rate of ammonia in aqueous solution. A possible cause of the increase in the ammonia decomposition rate with the addition of oxygen is enhancement of the charge separation efficiency. It is known that oxygen is a good electron acceptor in aqueous solution, and an electron generated by UV irradiation of TiO₂ could easily react with O₂ to give O₂^{•-}, with efficient consumption of the resulting photogenerated electron, thus preventing the accumulation of negative charge on the surface of the photocatalyst [15]. Recombination of the photogenerated electron and hole could be suppressed due to consumption of the electron by O₂, thus enhancing the ammonia oxidation rate by the hole. A similar observation, that the addition of oxygen increased the photooxidation rate of organic compounds in the aqueous phase using a TiO₂ photocatalyst, was reported by Hirakawa et al. [16].

To confirm whether charge separation efficiency affects the rate of ammonia decomposition, the reaction was conducted with the addition of silver nitrate, which acts as a sacrificial reagent for electrons, instead of oxygen (Fig. 4). The reaction was carried out under the condition of [NH₃]_i = 0.5 mM, because too much silver was loaded on the surface of the catalyst by photodeposition under the condition of [NH₃]_i = 5 mM. An increase in the ammonia decomposition rate was observed by addition of silver nitrate, and silver loaded on Pt-TiO₂ did not accelerate the decomposition rate. Thus, an increase in charge separation efficiency was concluded to be a contributor to the reaction.

When the reaction was conducted under N₂ flow, the concentration of ammonia decreased linearly with reaction time as shown in Fig. 1 and Fig. 4, which indicated that the decomposition rate was independent of the ammonia concentration. In the absence of

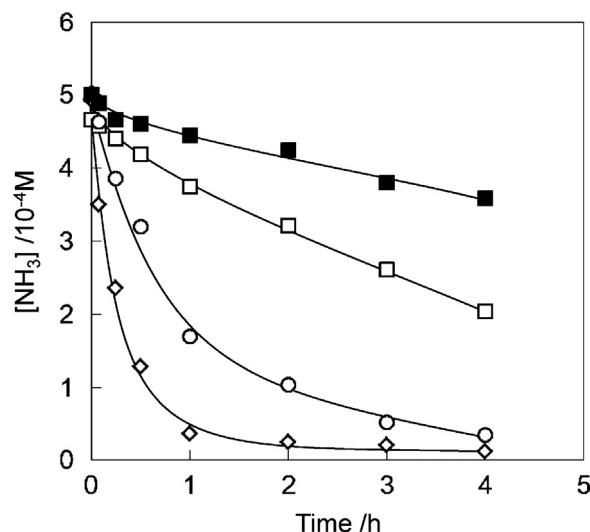


Fig. 4. Effect of the addition of air or silver nitrate. Catalyst: 0.5 wt% Pt-TiO₂ (○, ◇, □), 1 wt% Ag-0.5 wt% Pt-TiO₂ (■). (◇): silver nitrate was added (5 mM). The reactions were conducted under air (○) or N₂ (◇, □, ■).

oxygen, the photoinduced electron is considered to be consumed by water. This electron consumption step is relatively small and determines the rate of decomposition of ammonia. On the other hand, the rate of consumption of the photogenerated electron by oxygen is fast, such that the decomposition rate of ammonia depends on the ammonia concentration.

3.3. Influence of DO concentration decomposition rate of ammonia and selectivity

To examine the influence of DO concentration on the decomposition rate of ammonia and selectivity, we conducted reactions under different partial pressures of oxygen (PO₂). DO concentration at the beginning of each reaction ([DO]_i) increased from 0.03 mM to 0.80 mM when PO₂ was varied from 0 MPa to 0.1 MPa. Under air flow (PO₂ = 0.02 MPa), [DO]_i was 0.24 mM. As shown in Fig. 1, DO concentration decreased transiently in the initial stage of the reaction, and then increased up to [DO]_i and this concentration was maintained during the reaction. Fig. 5 shows the relationship between [DO]_i and the initial decomposition rate of ammonia. The initial decomposition rate increased with [DO]_i below 0.09 mM. The increase in decomposition rate was attributed to enhancement of the charge separation efficiency with increasing DO concentration. For [DO]_i above 0.09 mM, the initial decomposition rates were

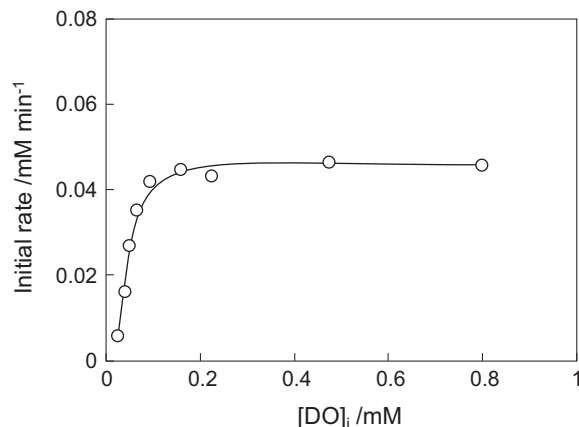


Fig. 5. Relationship between [DO]_i and initial decomposition rate of ammonia.

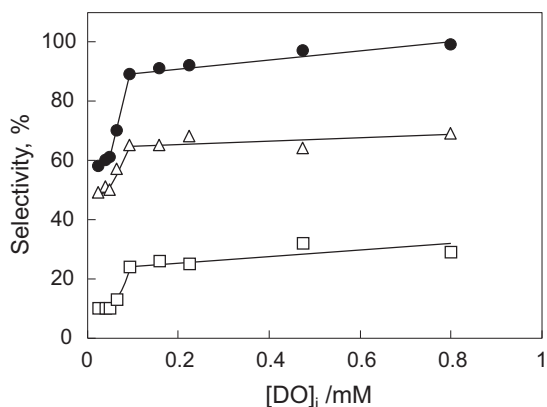
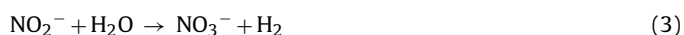
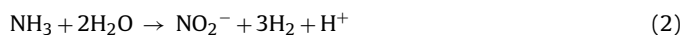


Fig. 6. Relationship between $[DO]_i$ and selectivity. Triangles: selectivity for nitrite; squares: nitrate; circles: sum of nitrite and nitrate.

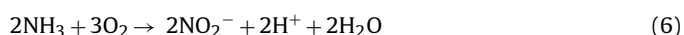
almost constant. In this region, it is considered that oxygen was dissolved sufficiently in the reaction solution and charge separation efficiency did not increase despite an increase in DO concentration.

Fig. 6 shows the relationship between $[DO]_i$ and selectivity for nitrate, nitrite, and the sum of nitrate and nitrite. The selectivity for nitrite and nitrate increased with $[DO]_i$ up to 0.09 mM, and was nearly constant for $[DO]_i$ over 0.09 mM.

Under N_2 flow, the selectivity for nitrite and nitrate was 37% and 5%, respectively, which indicated that some ammonia was photooxidized to nitrite and then further oxidized photocatalytically to nitrate in the absence of oxygen. The product was thought to be mainly dinitrogen as shown by Eq. (1), although its amount was not measured. Kaneko et al. [17] and Yoshida et al. [18] reported that hydrogen and dinitrogen were formed at a molar ratio of 1:3 by photodecomposition of ammonia over TiO_2 in the absence of oxygen. Thus, the reaction rate for Eq. (1) would be faster than that for Eq. (2) in the absence of oxygen.



In contrast, in the presence of oxygen, the reactions in which oxygen functions as an acceptor of photogenerated electrons seemed to proceed predominately as shown in Eqs. (4)–(7). Although the amounts of dinitrogen and nitrous oxide were not measured in this study, they were detected as products of the photocatalytic decomposition of gaseous ammonia over TiO_2 in the presence of oxygen [11].



Since the selectivity for the sum of nitrite and nitrate was over 90% for relatively high concentrations of DO (over 0.09 mM) as shown in Fig. 6, the reaction rate for Eq. (6) would be larger than that for Eqs. (4) or (5) in the presence of oxygen.

3.4. Influence of ammonia concentration on reaction rate and selectivity

Fig. 7 shows time courses of ammonia and DO concentrations under an air flow rate of $100\text{ cm}^3\text{ min}^{-1}$ for initial ammonia concentrations of 5–100 mM. In the beginning of each reaction, DO concentration decreased and then was maintained at about 0.2 mM.

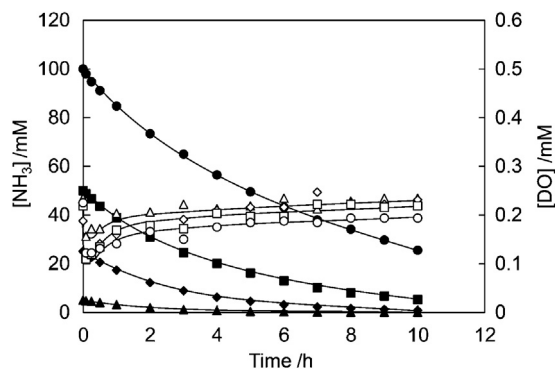


Fig. 7. Time courses of ammonia and DO concentrations in the presence of 0.5 wt% Pt- TiO_2 under air flow with different $[NH_3]_i$. $[NH_3]_i$: 5 mM (triangles), 25 mM (diamonds), 50 mM (squares), 100 mM (circles). Closed symbols: concentration of ammonia; open symbols: concentration of DO.

The decrease in ammonia concentration with reaction time was not linear even when the initial ammonia concentration was 100 mM. The slope of the double logarithmic plot of ammonia concentration and decomposition rate, corresponding to the reaction order, was 0.97 when the initial ammonia concentration was 100 mM. In addition, similar time courses of ammonia were obtained under air flow and oxygen flow at the condition of $[NH_3]_i = 100\text{ mM}$. These results indicate that oxygen was sufficiently supplied under $100\text{ cm}^3\text{ min}^{-1}$ air flow for efficient decomposition of 100 mM of ammonia.

Table 1 shows the selectivity of the products at 10 h for various initial concentrations of ammonia. The selectivities for nitrite and nitrate decreased with increasing initial concentrations of ammonia. While the selectivity for the sum of nitrate and nitrite under oxygen flow was larger than that under air flow at $[NH_3]_i = 100\text{ mM}$,

Table 1
Influence of initial ammonia concentration on selectivity.

$[NH_3]_i$ (mM)	Gas	Conversion (%)	Selectivity (%)		
			NO_2^-	NO_3^-	Sum of NO_2^- and NO_3^-
5	Air	100	63	29	92
25	Air	97	53	19	72
50	Air	90	50	16	66
100	Air	75	31	12	43
100	O_2	70	29	26	55

Reaction conditions: flow rate of gas $100\text{ cm}^3\text{ min}^{-1}$, reaction time 10 h.

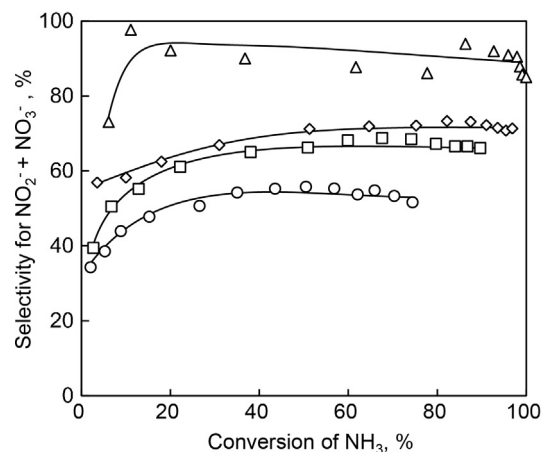


Fig. 8. Relationship between ammonia conversion and selectivity for nitrite and nitrate. $[NH_3]_i$: 5 mM (triangles), 25 mM (diamonds), 50 mM (squares), 100 mM (circles).

the difference was small. Fig. 8 shows the relationship between the conversion of ammonia and selectivity for nitrite and nitrate. In the initial stage of the reaction, i.e., up to 10% conversion, the selectivity for nitrite and nitrate was low and increased as the reaction proceeded. In contrast, the change in selectivity with increasing conversion was small as the reaction proceeded, i.e., over 30% conversion.

Thus, lower selectivity for nitrate and nitrite were obtained for higher initial concentrations of ammonia and lower conversion times. Since the time courses of DO under different initial concentrations of ammonia were not different as shown in Fig. 7, DO concentration did not affect the selectivity under $100\text{ cm}^3\text{ min}^{-1}$ air flow. It is considered that the decrease in selectivity for nitrate and nitrite equals the increase in selectivity for dinitrogen or nitrous oxide. Since the formation of dinitrogen or nitrous oxide is needed to combine the two N-containing species, the formation preferentially proceeds under higher density of N-species, such as under high ammonia concentration and low conversion conditions.

To determine the reaction products in the gas phase, an experiment was conducted under an O_2 flow rate of $5\text{ cm}^3\text{ min}^{-1}$ for initial ammonia concentrations of 100 mM. The concentration of DO during the reaction was about 0.7 mmol/L, and the amount of ammonia decomposed at 10 h was 31 mmol. The total amounts of nitrate, nitrite, nitrous oxide and dinitrogen formed at 10 h were 7.3 mmol, 10 mmol, 1.5 mmol, and 7.4 mmol, respectively. Since selectivity (N-atom base) for nitrous oxide and dinitrogen were 9.8% and 48%, respectively, and the N-balance was near one, it was indicated that the product, other than nitrate and nitrite, under this condition was mainly dinitrogen, which is the favored product.

4. Conclusions

The decomposition rate of aqueous ammonia over the Pt-TiO₂ photocatalyst was significantly increased by the addition of oxygen to the reaction system. The decomposition rate increased with increasing DO concentration between 0.03 and 0.09 mM due to the enhancement of charge separation efficiency. In the absence of oxygen, a longer reaction time was needed to decompose relatively high concentrations of aqueous ammonia because the reaction order for ammonia concentration was nearly zero. However, under the $100\text{ cm}^3\text{ min}^{-1}$ air flow ($[\text{DO}]_i = 0.24\text{ mM}$), the reaction order for ammonia concentration was 0.97 until $[\text{NH}_3]_i = 100\text{ mM}$, so that relatively high concentrations of ammonia could be decomposed in a shorter time. The main reaction products were nitrate and nitrite for $[\text{NH}_3]_i = 5.0\text{ mM}$ under air flow. However, the reaction was

suppressed as the concentration of ammonia increased. This implies that the density of N-containing intermediate species on the surface of a photocatalyst affects the selectivity of products.

The nitrite and nitrate selectivity obtained in the present study is not yet suitable for application to wastewater purification. It is still necessary to suppress the nitrite and nitrate selectivity, e.g., by optimizing the reaction conditions and improving the catalyst. However, it is expected that this photocatalytic decomposition can be applied to treatment of wastewater that contains relatively high concentrations of aqueous ammonia due to the significant increase in decomposition rate with the addition of oxygen.

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